Isotope tracing study on oxidation of water on photoirradiated TiO$_2$ particles

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ABSTRACT

Water is oxidized to molecular oxygen on a TiO$_2$ photocatalyst using electron acceptors such as Ag$^+$ and Fe^{3+} ions. However, there has been no information about whether this reaction occurs or not using molecular oxygen as the electron acceptor. We found by analysis of oxygen in the gas phase using ^{18}O-enriched water that this reaction does in fact occur. The quantum efficiency was higher with rutile-form particles than with anatase-form particles. O$_2$ was photocatalytically produced using O atoms supplied solely from water even in the presence of O$_2$ in the system. These results are important for deepening the understanding of TiO$_2$ photocatalysts because molecular oxygen is used most frequently as the electron acceptor and the intermediates of oxidation of water are involved in various kinds of photocatalytic reactions.

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1. Introduction

Usefulness of TiO$_2$ as a photocatalyst or a photoelectrode has been confirmed in splitting water for producing hydrogen, eliminating contaminants or harmful microbial organisms for environmental treatment, and selective conversion of chemical compounds [1–6]. In most of the applications, TiO$_2$ is used in the presence of O$_2$ and water molecules. The oxygen is used as an electron acceptor in the reaction systems carried out in both gas phase and aqueous solution. Water is used as a medium or solvent of reactions in liquid phase. Even in gas-phase reactions, water molecules adsorbed on TiO$_2$ photocatalysts plays an important role in the reactions. Therefore, it is important to clarify the behavior of O$_2$ and H$_2$O on photoirradiated TiO$_2$. Electrons and holes photo-generated in the conduction band and valance band of TiO$_2$, respectively, interact with O$_2$ and H$_2$O. As a result, species such as HO$^•$, O$_2^{•-}$ and H$_2$O$_2$ are produced [1–3,7–10]. These species are considered to be the origin of the strong oxidative property of TiO$_2$ photocatalysts under UV light. However, the details of formation of these active species on the surface of TiO$_2$ are still unclear. In fact, formation of free HO radicals from water on TiO$_2$ under UV irradiation is controversial [11,12].

In this work, by using ^{18}O-enriched water, we investigated production of O$_2$ from water on photoirradiated TiO$_2$ using O$_2$ as an electron acceptor. There is no net reaction except the exchange of O atoms between H$_2$O and O$_2$. However, it is important for the following reasons.

Firstly, it is important to clarify whether or not O$_2$ has the ability as an electron acceptor to oxidize water on TiO$_2$ photocatalysts because oxidation of water on TiO$_2$ photocatalysts depends on electron acceptors used in the systems. For example, Ag$^+$ ions are capable of oxidizing water when they are added to an aqueous solution containing TiO$_2$ particles under UV irradiation. On the other hand, protons are not capable of oxidizing water even when Pt is loaded on TiO$_2$ particles, except for cases with some special arrangements [13,14]. It is simply interesting to know whether or not water is oxidized using O$_2$ as an electron acceptor. Confirmation can be done only by using labeled water (H$_2$^{18}O).

The second important point is related to the mechanism of photocatalytic reactions of organic compounds on TiO$_2$ particles, which are usually carried out using O$_2$ as the electron acceptor. It is believed that OH radicals produced from surface hydroxyl groups on photoirradiated TiO$_2$ cause oxidative decomposition of organic compounds. If OH radicals are produced from water, it means that O$_2$ can also be produced from water in the system because hydrogen peroxide formed from two OH radicals is easily decomposed to O$_2$. Therefore, if O$_2$ is not produced from water using O$_2$ as an electron acceptor, the mechanism by OH radicals is excluded. As shown later, we found that O$_2$ is produced from water using O$_2$ as an electron acceptor. However, it should be noted that this does not necessarily mean that OH radical is produced from water because O$_2$ can be produced from water via intermediates other than OH radical.

Lastly, the efficiency of O$_2$ production from water using O$_2$ as an electron acceptor and using different kinds of TiO$_2$ particles is also interesting. It is known that TiO$_2$ particles having high activity for oxidation of water often do not show high activity for decomposition of organic compounds. More precisely, rutile particles are less

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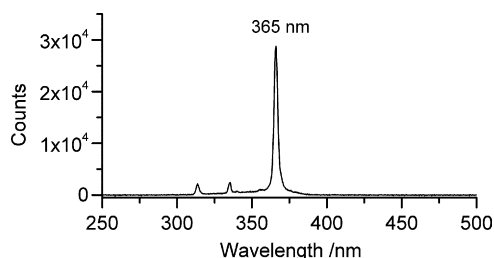*E-mail address:* matsu@chem.es.osaka-u.ac.jp (M. Matsumura).

Fig. 1. Spectral distribution of UV light used for photocatalytic reactions.

active for decomposition of organic compounds than are anatase particles, while rutile particles are more active for oxidation of water than are the anatase particles [15,16]. These tendencies may be caused by the different electron acceptors used for evaluation of the activities: O_2 is used for the decomposition of organic molecules and Ag^+ or Fe^{3+} ions are used in most cases for the oxidation of water. If oxidation of water is more active with rutile particles than with anatase particles even by using O_2 as the electron acceptor, which can be confirmed by using labeled water, we can conclude that there is an essential difference in the oxidation mechanisms. We found this to be the case: O_2 evolved more efficiently on rutile particles than on anatase particles using O_2 as the electron acceptor.

2. Experimental

Different kinds of titanium dioxide powders were used as photocatalysts. They were HT0514 (100% rutile, specific area of 6.5 m^2/g) obtained from Toho Titanium, and PT101 (100% rutile, 25 m^2/g), ST-41 (100% anatase, 8.2 m^2/g) and ST-01 (100% anatase, 192 m^2/g) obtained from Ishihara Sangyo. In some experiments, Pt-black powder (fuel cell grade, >99.9%, Sigma–Aldrich) was loaded on TiO_2 photocatalysts by mechanically mixing them with an agate mortar. Water containing 10% $H_2^{18}O$ was purchased from Cambridge Isotope Laboratories, Inc. and used as the labeled oxygen source.

Photocatalytic reactions were carried out in ^{18}O-enriched water (2 mL) in a closed Pyrex tube (16 mL). The gas phase in the reaction tube was filled with normal air. Titanium dioxide powder (20 mg) was suspended in the water with a magnetic stirrer and irradiated with UV light. The UV light was selected from the beam from a 500 W super pressure mercury lamp (Wacom, BMO-500DY) using a band-pass filter (Kenko, BP-365) and had the highest intensity at a wavelength of 365 nm, as shown in Fig. 1. The spectrum was measured with a UV–vis spectrometer (Ocean Optics, USB4000). Intensity of the UV light was controlled to be different levels by inserting fine stainless meshes in the light beam and was monitored with a thermopile (Eppley Laboratory). The content of labeled oxygen evolved in the gas phase was analyzed with a gas chromatograph (GC-2010 Shimadzu) equipped with a mass analyzer (GCMP-2014S Shimadzu).

From the amount of O_2 molecules evolved and number of photons irradiated, apparent quantum efficiency (AQE) of the reaction can be determined. Although we used ^{18}O-enriched water, we can neglect a very small isotopic effect on the reaction rate of O_2 production. Since two holes are necessary for evolution of one O atom in O_2 and the content of $H_2^{18}O$ in the water used was 10%, AQE of photocatalytic oxidation of water is defined as

$$\text{AQE} = \frac{[\text{number of holes used for photooxidation of } H_2O]}{[\text{number of photons irradiated}]}$$

$$= \frac{[\text{number of } ^{18}O \text{ atoms included in evolved } O_2] \times 20}{[\text{photon flux}] \times [\text{area}] \times [\text{irradiation time}]} \quad (1)$$
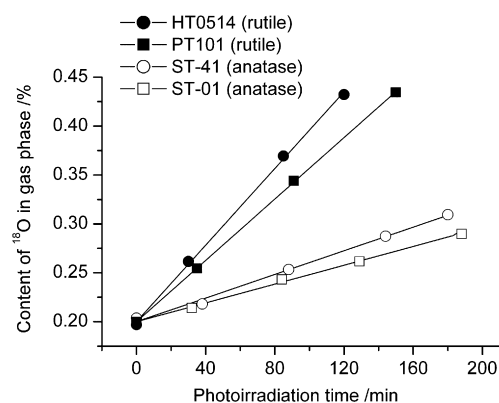

Fig. 2. Change in content of ^{18}O in O_2 in the gas phase during photoirradiation of TiO_2 particles suspended in labeled water (10% $H_2^{18}O$). The four lines represent the 4 kinds of TiO_2 particles used. Photon flux was 4.0×10^{16} s^{-1} cm^{-2}, and area of photoirradiation was 1.7 cm^2.

3. Results

We analyzed O_2 ($^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$) in the gas phase by periodically sampling a small portion of the gas from the reaction tube during photoirradiation of the suspension containing labeled water (10% $H_2^{18}O$) and rutile (HT0514 or PT101) or anatase (ST-41 or ST-01) powder. The gas phase in the reaction tube initially contained normal air (14 mL); the natural abundance of ^{18}O in oxygen is about 0.2%. Since the reaction produces O_2 and also consumes O_2, the reaction does not cause changes in the total amount of O_2 in the gas phase, if we neglect production of small amounts of intermediate species. However, the content of ^{18}O in O_2 in the gas phase, which is defined as $(^{16}O^{18}O + 2 \times {}^{18}O_2)/[2 \times ({}^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2)]$, increased with irradiation time, as shown in Fig. 2. No change was observed in the content of ^{18}O in the absence of either TiO_2 powder or UV light. Therefore, the increase in the content of ^{18}O in O_2 in the gas phase suggests that photocatalytic O_2 production and O_2 consumption take place on TiO_2 under UV irradiation. If the reaction time is prolonged, the content of ^{18}O in the gas phase will approach 10% because the total amount of O atoms included in the system is mostly determined by the amount of O atoms included in the water, which contains 10% $H_2^{18}O$. However, during reactions shown in Fig. 2, the contents of ^{18}O in the gas phase were less than 0.45% and the slopes were linear. This indicates that reduction of O_2 that were produced from water was negligible during the time period. From the slopes of the lines, the flux of photons irradiated (4.0×10^{16} s^{-1} cm^{-2}), and the area of photoirradiation (1.7 cm^2), we can estimate AQE of oxidation of water using Eq. (1). The determined AQE values for HT0514 (rutile), PT101 (rutile), ST-41 (anatase) and ST-01 (anatase) were 1.35, 1.08, 0.42 and 0.33%, respectively. The AQE values for the rutile particles are about 3-times higher than those of the anatase particles. The larger particles showed higher efficiency for both rutile and anatase particles. These tendencies were almost the same as the tendencies for oxidation of water using Ag^+ ions or Fe^{3+} ions as the electron acceptor [16,17]. Concerning oxidation of organic compounds, such as ethanol, it is well known that small anatase particles show much higher activity using O_2 as the electron acceptor [18]. Hence, the different tendencies for oxidation of water and oxidation of organic compounds suggest that there is an essential difference in these oxidation processes.

AQE for O_2 production from water decreased with increase in light intensity, as shown by the solid line in Fig. 3. Similar dependence on photon flux has been reported for oxidation of organic compounds. The behavior was attributed to decrease in the amount of reactants adsorbed on TiO_2 particles under the condition of
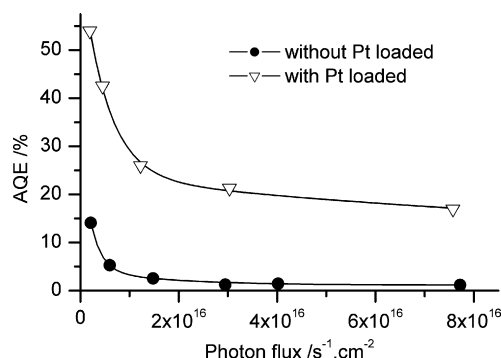
Fig. 3. Dependence of AQE of O_2 production from water on UV light intensity. HT0514 particles (rutile) were used as the photocatalyst: closed circles without Pt loading and open triangles with Pt (4 wt%) loading. The flux of photons irradiated was adjusted using stainless meshes. Area of photoirradiation was 1.7 cm^2.

phtocatalytic reactions [19]. Another explanation for the reaction efficiency depending on photon flux is that the reaction efficiency is affected by the electron-hole recombination through intermediate species including trapped holes [12].

AQE for oxidation of water was increased by loading the TiO_2 (HT0514) particles with fine platinum particles, as shown by the broken line in Fig. 3. Interestingly, AQE for the Pt-loaded TiO_2 particles was maintained at a level higher than 15% even under strong irradiation. These properties are attributed to the accelerated electron transfer from TiO_2 to O_2 due to the catalytic effect of Pt for the reduction of O_2. This allows maintenance of the band bending of TiO_2 during the photocatalytic reaction, which is needed for oxidation of water. A similar effect was reported for the case of Pt-loaded CdS particles, on which protons are reduced and sulfite ions are oxidized [20].

It is important to examine the possibility of the involvement of O_2 molecules in the process of water oxidation into O_2. The point is whether O_2 molecules react with the intermediates produced from water. If O_2 is produced only from water molecules, $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ must be produced in the ratio of 81:18:1 because we used labeled water containing 10% $H_2^{18}O$. On the other hand, if O_2 reacts with the intermediate species, the contribution of ^{16}O must be increased. In this experiment, we could not determine the amount of $^{16}O_2$ produced from water because a large amount of $^{16}O_2$ was included in the gas phase, which was air. However, we could determine the ratio of $^{16}O^{18}O$ to $^{18}O_2$ produced because the natural abundance of ^{18}O is small. Fig. 4 shows that the ratio is 18:1, indicating that O_2 is produced photocatalytically using O atoms supplied solely from water. In other words, the result excludes
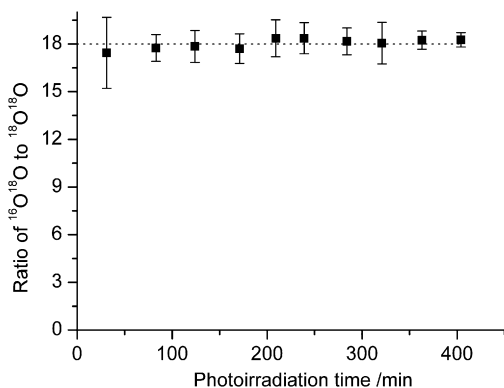
mechanisms in which atomic exchange between O_2 (and $O_2^{\bullet-}$) and active species formed from water on the surface of TiO_2, such as Ti—$O^\bullet$ and Ti—O—$O^\bullet$, is involved.

4. Discussion

The experimental results obtained are important when we discuss the source of oxygen introduced into the products of photocatalytic reactions. For example, we found that when benzene is converted to phenol on TiO_2 photocatalysts, a part of the oxygen introduced into phenol comes from O_2 molecules [21]. The absence of O exchange between O_2 and surface active species on TiO_2, which is concluded from the results shown in Fig. 4, indicates that phenol containing an O atom from O_2 is produced as a result of reaction between activated benzene (probably benzene cation radical) and O_2 (or $O_2^{\bullet-}$). On the other hand, the presence of phenol having an O atom supplied from H_2O indicates that the phenol is also produced by the reaction between benzene and intermediate species produced from H_2O or between activated benzene (benzene cation radical) and H_2O.

The absence of O-atom exchange between O_2 and the intermediate species formed on TiO_2 is also important when we discuss the mechanism of oxidation of water. Although this is a basic reaction, oxidation of water into O_2 on a TiO_2 photocatalyst is a very complicated reaction. When water molecules are oxidized into molecular oxygen, 4 electrons must be removed from 2 water molecules, as expressed by Eq. (2).

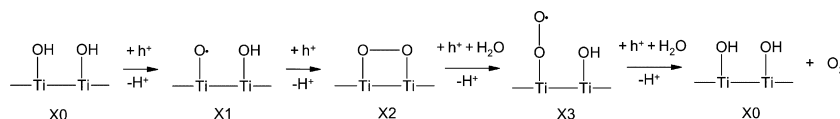$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \qquad (2)$$

The reaction is expected to proceed sequentially via 3 intermediate states starting from the initial state, which is schematically illustrated in Scheme 1. The 4 states are expressed by X0, X1, X2, and X3. There are many possibilities for the atomic configurations of the 4 states. For example, X1 can be OH radicals, surface trapped holes, or holes trapped by lattice O atoms [22]. The modes shown in Scheme 1 are the simplest examples.

The result obtained from Fig. 4 indicates that there is no exchange of O atoms between the surface species of the intermediates and O_2. This means that O atoms in the active species are supplied only by water (or hydroxyl ion). The process shown in Scheme 1 is related to the reaction of organic compounds on TiO_2 photocatalysts as discussed below.

The fact that production of O_2 and decomposition of organic compounds show different dependence on the crystalline forms of TiO_2 (rutile and anatase) arises from the different reaction paths for these processes. For O_2 production, the process shown in Scheme 1 must be completed. On the other hand, the intermediate states X1, X2 and X3 can be active species for the reaction with organic compounds. This difference is attributed to different preference of the reactions for TiO_2 particles having different surface atomic configurations. Of these intermediates, we consider that X1, which can be an analogue of OH radical, is most responsible for the reaction because its radical character causes high reactivity toward organic compounds. It is reasonable to assume that TiO_2 particles having high activity for producing O_2 from water can forward all of the steps shown in Scheme 1 at high efficiency. However, the efficient transition from X1 to X2 adversely affects oxidation of organic compounds via the X1 state. This gives a general explanation for why oxidation of water and oxidation of organic compounds show different preference for TiO_2 particles, although it is difficult to clarify the exact mechanism.

Generally, production of O_2 from water is more difficult than oxidation of organic compounds on TiO_2 particles. This is attributed to the fact that a larger amount of intermediates states (X1, X2 and X3) need to be formed for oxidation of water; the X2 state

Fig. 4. Ratio of $^{16}O^{18}O$ to $^{18}O^{18}O$ accumulated in the gas phase during photoirradiation of TiO_2 particles (HT0514) (rutile) suspended in labeled water (10% $H_2^{18}O$). Photon flux was 4.0×10^{16} s^{-1} cm^{-2}, and area of photoirradiation was 1.7 cm^2.

Scheme 1. Examples of 4 states formed successively before an oxygen molecule is generated on the surface of TiO_2.

is expected to accumulate most because of its chemical stability. These intermediates can be recombination centers, which accept electrons from the conduction band and shift back the sequential process of Scheme 1. The lower efficiency of production of O_2 than oxidation of organic compounds is therefore attributed to the involvement of these intermediates in O_2 production.

The fact that large particles showed higher activity for oxidation of water using either rutile or anatase particles suggests that special separation of electrons and holes in a particle is important to reduce electron-hole recombination. In some cases, the separation is visualized by deposition of oxidative and reductive products on different sites of a photocatalyst particle [23].

5. Conclusions

By tracing oxygen-18 isotope in photocatalytic reactions, we confirmed that oxidation of water occurs on the TiO_2 surface under UV irradiation using O_2 as the electron acceptor. In reactions for oxidizing organic materials on TiO_2 photocatalysts, O_2 is commonly used as the electron acceptor. Hence, the results indicate that the intermediates of O_2 evolution from water can be active species for the oxidation of organic compounds on TiO_2 photocatalysts. However, only the initial intermediate(s) in oxidation of water can be used for the oxidation of organic compounds. This leads to different tendencies of the activity of photocatalysts used for oxidation of organic compounds and water.

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